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(54) PIEZOELECTRIC ELEMENT MATERIAL AND ITS PRODUCTION**(57) Abstract**

PURPOSE: To enable sintering even at a low temp. by using Pb-contg. ceramics having a specified average grain size and a specified grain size distribution and to obtain a piezoelectric element material having improved piezoelectric characteristics of piezoelectric ceramics by controlling the fine structure of the Pb-contg. ceramics.

CONSTITUTION: This piezoelectric element material contains Pb-contg. ceramics having 0.5-5 μ m average grain size and a grain size distribution in which \approx 90wt.% grains are within the range of 0.5-5 μ m. The basic compsn. of this material is preferably represented by the general formula $Pb_{1-x}Sr_x(Mg_{1/3}Nb_{2/3})_aTi_bZr_cO_3$ (where $a+b+c=1$, $0.20 \leq a \leq 0.30$, $0.30 \leq b \leq 0.45$, $0.30 \leq c \leq 0.40$ and $0.01 \leq x \leq 0.20$) and 0.01-0.2wt.% Fe_2O_3 is preferably added to the basic compsn.

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(54) 【発明の名称】 圧電素子材料及びその製造方法

(57) 【要約】

【目的】 低温で焼結でき、焼結性がよく、その微細構造を制御した圧電セラミックスとその製造方法を提供する。

【構成】 圧電セラミックス粉末として組成が $Pb_{0.9}Sr_{0.1}(Mg_{1/3}Nb_{2/3})_{0.255}Ti_{0.35}Zr_{0.355}$ 、及び $Pb(Ni_{1/3}Nb_{2/3})_{0.45}Ti_{0.35}Zr_{0.3}$ O_3 など原料粉末を媒体攪拌ミルを用いて、直径0.6mmのジルコニア玉石と共に、有機系の分散剤及び水を加え、平均粒子径約0.2 μm に粉碎したのち乾燥させ、造粒した。この粉体を、金型を用いて直径13mm、厚さ約1mmの円板状の成形体を作製し、通常の焼成温度よりも低温で2時間焼成し、微細構造を制御した圧電セラミックスを製造する。

【特許請求の範囲】

【請求項1】 セラミックスの平均結晶粒径が0.5～5μmであり、かつ前記平均粒径の粒子が90重量%以上0.5～5μmの間に分布するPb系セラミックスを含む圧電素子材料。

【請求項2】 平均結晶粒径が1～3μmであり、かつ前記平均結晶粒径の粒子が75重量%以上1～3μmの間に分布するPb系セラミックスを含む請求項1に記載の圧電素子材料。

【請求項3】 圧電素子材料組成が一般式 $Pb_{1-x}Sr_x(Mg_{1/3}Nb_{2/3})_yTi_zZr_{1-y-z}O_3$ で示され、
(但し $A+B+C=1$)

$$0.20 \leq A \leq 0.30$$

$$0.30 \leq B \leq 0.45$$

$$0.30 \leq C \leq 0.40$$

$$0.01 \leq x \leq 0.20$$

を満足する基本組成を主成分とする請求項1または2に記載の圧電素子材料。

【請求項4】 Fe_2O_3 を0.01～0.2重量%の範囲存在させる請求項3に記載の圧電素子材料。

【請求項5】 組成が一般式 $Pb(Ni_{1/3}Nb_{2/3})_yTi_zZr_{1-y-z}O_3$ で示され、
(但し $A+B+C=1$)

$$0.40 \leq A \leq 0.55$$

$$0.15 \leq B \leq 0.30$$

$$0.10 \leq C \leq 0.30$$

を満足する基本組成を主成分とする請求項1に記載の圧電素子材料。

【請求項6】 Fe_2O_3 を0.01～0.5重量%の範囲存在させる請求項5に記載の圧電素子材料。

【請求項7】 組成が一般式 $Pb_{1-x}Sr_x(Ni_{1/3}Nb_{2/3})_yTi_zZr_{1-y-z}O_3$ で示され、
(但し $A+B+C=1$)

$$0.35 \leq A \leq 0.55$$

$$0.15 \leq B \leq 0.40$$

$$0.15 \leq C \leq 0.40$$

$$0.01 \leq x \leq 0.10$$

を満足する基本組成を主成分とする請求項1または2に記載の圧電素子材料。

【請求項8】 Fe_2O_3 を0.01～0.5重量%の範囲存在させる請求項5に記載の圧電素子材料。

【請求項9】 一般式 $Pb(Ni_{1/3}Ta_{2/3})_yTi_zZr_{1-y-z}O_3$ で示され、
(但し $A+B+C=1$)

$$0.25 \leq A \leq 0.45$$

$$0.20 \leq B \leq 0.35$$

$$0.20 \leq C \leq 0.40$$

を満足する基本組成を主成分とする圧電素子材料に対して、Pbの一部分を、アルカリ土類金属及び希土類元素のなかから選ばれた少なくとも1種の金属で0.01～0.2モル%置換し、かつ副成分として、 Fe_2O_3 を0.01～0.5重量%存在させた請求項1または2に

記載の圧電素子材料。

【請求項10】 組成が一般式 $Pb_{1-x}Sr_x(Mg_{1/3}Nb_{2/3})_y(Ni_{1/3}Nb_{2/3})_zTi_wZr_{1-y-z-w}O_3$ または、 $Pb_{1-x}Sr_x(Mg_{1/3}Nb_{2/3})_y(Ni_{1/3}Ta_{2/3})_zTi_wZr_{1-y-z-w}O_3$ または $Pb(Ni_{1/3}Nb_{2/3})_y(Ni_{1/3}Ta_{2/3})_zTi_wZr_{1-y-z-w}O_3$ で示され、
(但し $A+B+C+D=1$)

$$0.05 \leq A \leq 0.55$$

$$0.05 \leq B \leq 0.55$$

$$0.15 \leq C \leq 0.30$$

$$0.15 \leq D \leq 0.30$$

$$0.01 \leq x \leq 0.20$$

を満足する基本組成を主成分とする圧電素子材料に対して、副成分として、希土類元素の酸化物から選ばれた少なくとも1種を0.01～0.5重量%、及び Fe_2O_3 を0.05～0.5重量%添加含有してなる請求項1または2に記載の圧電素子材料。

【請求項11】 粉体の平均粒子径が0.4μm以下で、かつ前記粉体の粒度分布が前記平均粒子径の2倍以上の大きさの粒子の割合を7重量%以上含む微粉体を焼結前原料粉体として用い、焼結前原料粉体を焼結してセラミックスの平均結晶粒径が0.5～5μm、かつ前記平均粒径の粒子が90重量%以上0.5～5μmの間に分布するPb系セラミックスを含む圧電素子材料を得る圧電素子材料の製造方法。

【請求項12】 粉体煤液の体積が粉体の真の体積の4倍以下の量でかつ分散剤を添加して粉砕し、かつ0.6mm以下の微小な玉石を用いた請求項11に記載の圧電素子材料の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、精密機械の位置決め、ビデオオートトラッキング用圧電アクチュエーター、セラミックフィルタ、セラミック発振子等の圧電素子、赤外線センサー、リニアアレイセンサー等の焦電素子等の用途に用いられる圧電セラミックス及び電歪セラミックス等の圧電素子材料に関するものである。

【0002】

【従来の技術】 強誘電性セラミックスまたは圧電セラミックスとしては、従来より $Pb(Ti, Zr)O_3$ 、二成分系、 $Pb(Mg_{1/3}Nb_{2/3})_xTi_yZr_{1-x-y}O_3$ 、三成分系、 $Pb(Zn_{1/3}Nb_{2/3})_x(Sn_{1/3}Nb_{2/3})_yTi_zZr_{1-x-y-z}O_3$ 、四成分系組成等より成るセラミックス材料がある。これらの従来のセラミックス材料は、その構成成分がほとんど全部がセラミックスであり、原料あるいは仮焼粉末を所定の形状に成形したのち、高温で焼成して作製される。これら従来の圧電セラミックスでは成分の組成比を選ぶことにより用途に応じて種々の特性の圧電セラミックスが作製され、アクチュエーター、セラミックフィルタ、圧電ブザー、圧電点火

栓、超音波振動子などの用途に用いられている。

【0003】

【発明が解決しようとする課題】従来の圧電セラミックスは、その作製上PbOの蒸発や2次相の生成などが免れず、十分その材料系が持つ特性を示すセラミックスが得られていなかった。とくに焼結性を阻害するような元素例えばSr等のアルカリ土類元素を含む場合などに十分緻密な焼結体が得られず、その材料が持つ特性を十分発揮することは、困難であった。そこで、その焼結性を向上させ、微細な構造を制御することは、優れた特性を持ったセラミックスを得るために必要なことである。

【0004】本発明は、前記従来の問題を解決するため、低温でも焼結でき、その微細構造を制御して圧電セラミックスの圧電特性を向上した圧電素子材料及びその製造方法を提供することを目的とする。

【0005】

【課題を解決するための手段】前記目的を達成するため、本発明の圧電素子材料は、セラミックスの平均結晶粒径が0.5~5μmであり、かつ前記平均粒径の粒子が90重量%以上0.5~5μmの間に分布するPb系セラミックスを含むという構成を備えたものである。

【0006】前記構成においては、平均結晶粒径が1~3μmであり、かつ前記平均結晶粒径の粒子が75重量%以上1~3μmの間に分布するPb系セラミックスを含むことが好ましい。

【0007】また前記構成においては、圧電素子材料組成が一般式 $Pb_{1-x}Sr_x(Mg_{1/3}Nb_{2/3})_A Ti_1 B C Zr_0 O_3$ で示され、(但し $A+B+C=1$)

$$0.20 \leq A \leq 0.30$$

$$0.30 \leq B \leq 0.45$$

$$0.30 \leq C \leq 0.40$$

$$0.01 \leq x \leq 0.20$$

を満足する基本組成を主成分とすることが好ましい。

【0008】また前記構成においては、 Fe_2O_3 を0.01~0.2重量%の範囲存在させることが好ましい。また前記構成においては、組成が一般式 $Pb(Ni_{1/3}Nb_{2/3})_A Ti_1 B C Zr_0 O_3$ で示され、(但し $A+B+C=1$)

$$0.40 \leq A \leq 0.55$$

$$0.15 \leq B \leq 0.30$$

$$0.10 \leq C \leq 0.30$$

を満足する基本組成を主成分とすることが好ましい。

【0009】また前記構成においては、 Fe_2O_3 を0.01~0.5重量%の範囲存在させることが好ましい。また前記構成においては、組成が一般式 $Pb_{1-x}Sr_x(Ni_{1/3}Nb_{2/3})_A Ti_1 B C Zr_0 O_3$ で示され、(但し $A+B+C=1$)

$$0.35 \leq A \leq 0.55$$

$$0.15 \leq B \leq 0.40$$

$$0.15 \leq C \leq 0.40$$

$$0.01 \leq x \leq 0.10$$

を満足する基本組成を主成分とすることが好ましい。

【0010】また前記構成においては、 Fe_2O_3 を0.01~0.5重量%の範囲存在させることが好ましい。また前記構成においては、一般式 $Pb(Ni_{1/3}Ta_{2/3})_A Ti_1 B C Zr_0 O_3$ で示され、(但し $A+B+C=1$)

$$0.25 \leq A \leq 0.45$$

$$0.20 \leq B \leq 0.35$$

$$0.20 \leq C \leq 0.40$$

を満足する基本組成を主成分とする圧電素子材料に対して、Pbの一部分を、アルカリ土類金属及び希土類元素のなかから選ばれた少なくとも1種の金属で0.01~0.2モル%置換し、かつ副成分として、 Fe_2O_3 を0.01~0.5重量%存在させることが好ましい。

【0011】また前記構成においては、組成が一般式 $Pb_{1-x}Sr_x(Mg_{1/3}Nb_{2/3})_A(Ni_{1/3}Nb_{2/3})_B Ti_1 C Zr_0 O_3$ または、 $Pb_{1-x}Sr_x(Mg_{1/3}Nb_{2/3})_A(Ni_{1/3}Ta_{2/3})_B Ti_1 C Zr_0 O_3$ または $Pb(Ni_{1/3}Nb_{2/3})_A(Ni_{1/3}Ta_{2/3})_B Ti_1 C Zr_0 O_3$ で示され、(但し $A+B+C+D=1$)

$$0.05 \leq A \leq 0.55$$

$$0.05 \leq B \leq 0.55$$

$$0.15 \leq C \leq 0.30$$

$$0.15 \leq D \leq 0.30$$

$$0.01 \leq x \leq 0.20$$

を満足する基本組成を主成分とする圧電素子材料に対して、副成分として、希土類元素の酸化物から選ばれた少なくとも1種を0.01~0.5重量%、及び Fe_2O_3 を0.05~0.5重量%添加含有してなることが好ましい。

【0012】次に本発明の圧電素子材料の製造方法は、粉体の平均粒径が0.4μm以下で、かつ前記粉体の粒度分布が前記平均粒径の2倍以上の大きさの粒子の割合を7重量%以上含む微粉体を焼結前原料粉体として用い、焼結前原料粉体を焼結してセラミックスの平均結晶粒径が0.5~5μm、かつ前記平均粒径の粒子が90重量%以上0.5~5μmの間に分布するPb系セラミックスを含む圧電素子材料を得るという構成を備えたものである。

【0013】前記構成においては、粉体媒液の体積が粉体の真の体積の4倍以下の量でかつ分散剤を添加して粉碎し、かつ0.6mm以下の微小な玉石を用いたことが好ましい。

【0014】

【作用】前記本発明の圧電素子材料の構成によれば、セラミックスの平均結晶粒径が0.5~5μmであり、かつ前記平均粒径の粒子が90重量%以上0.5~5μmの間に分布するPb系セラミックスを含むことにより、

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圧電セラミックスの圧電特性、たとえば圧電定数 d_{31} の絶対値が大きく、他の圧電定数 d_{12} 及び d_{15} の値も大きい圧電セラミックスを得ることができる。

【0015】前記において、平均結晶粒径が $1\sim 3\mu\text{m}$ であり、かつ前記平均結晶粒径の粒子が75重量%以上 $1\sim 3\mu\text{m}$ の間に分布するPb系セラミックスを含むという好ましい構成によれば、粒界部に存在する気孔の大きさが緻密なセラミックスの場合、その結晶粒子径に依存して十分小さくなるか、または非常にその数も減少し、材料の持つ特性を十分に発揮することができる。

【0016】また前記において、圧電素子材料組成が一般式 $\text{Pb}_{1-x}\text{Sr}_x(\text{Mg}_{1/3}\text{Nb}_{2/3})_A\text{Ti}_B\text{Zr}_C\text{O}_3$ で示され、(但し $A+B+C=1$)

$$0.20 \leq A \leq 0.30$$

$$0.30 \leq B \leq 0.45$$

$$0.30 \leq C \leq 0.40$$

$$0.01 \leq x \leq 0.20$$

を満足する基本組成を主成分とするという好ましい構成によれば、モルフォトピック フェイズ バウンダリ付近の組成となり、比誘電率 ϵ_r 、及び電気機械結合係数 k_p 及び k_{31} が大きく、圧電定数 d_{31} の絶対値の大きな材料を得ることができる。

【0017】また前記において、 Fe_2O_3 を0.01~0.2重量%の範囲存在させるという好ましい構成によれば、焼成温度が低下する分より微細な結晶粒子径を持ちかつ緻密なセラミックスが得られ、圧電定数の絶対値の大きな材料を得ることができる。

【0018】また前記構成において、組成が一般式 $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})_A\text{Ti}_B\text{Zr}_C\text{O}_3$ で示され、(但し $A+B+C=1$)

$$0.40 \leq A \leq 0.55$$

$$0.15 \leq B \leq 0.30$$

$$0.10 \leq C \leq 0.30$$

を満足する基本組成を主成分とするという好ましい構成によれば、モルフォトピック フェイズ バウンダリ付近の組成となり、比誘電率 ϵ_r 、及び電気機械結合係数 k_p 及び k_{31} が大きく、圧電定数 d_{31} の絶対値の大きな材料を得ることができる。

【0019】また前記において、 Fe_2O_3 を0.01~0.5重量%の範囲存在させるという好ましい構成によれば、焼成温度が低下する分より微細な結晶粒子径を持ちかつ緻密なセラミックスが得られ、圧電定数の絶対値の大きな材料を得ることができる。

【0020】また前記構成において、組成が一般式 $\text{Pb}_{1-x}\text{Sr}_x(\text{Ni}_{1/3}\text{Nb}_{2/3})_A\text{Ti}_B\text{Zr}_C\text{O}_3$ で示され、(但し $A+B+C=1$)

$$0.35 \leq A \leq 0.55$$

$$0.15 \leq B \leq 0.40$$

$$0.15 \leq C \leq 0.40$$

$$0.01 \leq x \leq 0.10$$

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を満足する基本組成を主成分とするという好ましい構成によれば、キュリー点が下がる分比誘電率の値が大きくなり、かつモルフォトピックフェイズ バウンダリ付近の組成となり、圧電定数 d_{31} の絶対値の大きな材料を得ることができる。

【0021】また前記において、 Fe_2O_3 を0.01~0.5重量%の範囲存在させるという好ましい構成によれば、焼成温度が低下する分より微細な結晶粒子径を持ちかつ緻密なセラミックスが得られ、圧電定数の絶対値の大きな材料を得ることができる。

【0022】また前記において、一般式 $\text{Pb}(\text{Ni}_{1/3}\text{Ta}_{2/3})_A\text{Ti}_B\text{Zr}_C\text{O}_3$ で示され、(但し $A+B+C=1$)

$$0.25 \leq A \leq 0.45$$

$$0.20 \leq B \leq 0.35$$

$$0.20 \leq C \leq 0.40$$

を満足する基本組成を主成分とする圧電素子材料に対して、Pbの一部分を、アルカリ土類金属及び希土類元素のなかから選ばれた少なくとも1種の金属で0.01~0.2モル%置換し、かつ副成分として、 Fe_2O_3 を0.01~0.5重量%存在させるという好ましい構成によれば、モルフォトピック フェイズバウンダリ付近の組成となり、比誘電率 ϵ_r 、及び電気機械結合係数 k_p 及び k_{31} が大きく、圧電定数 d_{31} の絶対値の大きな材料を得ることができる。

【0023】また前記において、組成が一般式 $\text{Pb}_{1-x}\text{Sr}_x(\text{Mg}_{1/3}\text{Nb}_{2/3})_A(\text{Ni}_{1/3}\text{Nb}_{2/3})_B\text{Ti}_C\text{Zr}_D\text{O}_3$ または、 $\text{Pb}_{1-x}\text{Sr}_x(\text{Mg}_{1/3}\text{Nb}_{2/3})_A(\text{Ni}_{1/3}\text{Ta}_{2/3})_B\text{Ti}_C\text{Zr}_D\text{O}_3$ または $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})_A(\text{Ni}_{1/3}\text{Ta}_{2/3})_B\text{Ti}_C\text{Zr}_D\text{O}_3$ で示され、(但し $A+B+C+D=1$)

$$0.05 \leq A \leq 0.55$$

$$0.05 \leq B \leq 0.55$$

$$0.15 \leq C \leq 0.30$$

$$0.15 \leq D \leq 0.30$$

$$0.01 \leq x \leq 0.20$$

を満足する基本組成を主成分とする圧電素子材料に対して、副成分として、希土類元素の酸化物から選ばれた少なくとも1種を0.01~0.5重量%、及び Fe_2O_3 を0.05~0.5重量%添加含有してなるという好ましい構成によれば、前記と同様、圧電定数 d_{31} の絶対値の大きな材料を得ることができる。

【0024】次に本発明の圧電素子材料の製造方法の構成によれば、粉体の平均粒子径が $0.4\mu\text{m}$ 以下で、かつ前記粉体の粒度分布が前記平均粒子径の2倍以上の大きさの粒子の割合を7重量%以上含む微粉体を焼結前原料粉体として用い、焼結前原料粉体を焼結してセラミックスの平均結晶粒径が $0.5\sim 5\mu\text{m}$ 、かつ前記平均粒径の粒子が90重量%以上 $0.5\sim 5\mu\text{m}$ の間に分布す

るPb系セラミックスを含む圧電素子材料を得ることにより、前記本発明の圧電素子材料を効率良く合理的に製造することができる。

【0025】前記において、粉体媒液の体積が粉体の真の体積の4倍以下の量でかつ分散剤を添加して粉碎し、かつ0.6mm以下の微小な玉石を用いたという好ましい構成によれば、高濃度媒液でありながら流動性が良好な媒液であるので、均質性に優れ、微小な玉石を用いているため、接触表面積も増え、また通常の粉碎時間では困難な粒径まで微粉碎できる。また、圧電セラミックスの平均結晶粒径が1~5μm以下であり、均一な組織よりなるようにするのが好ましい。また、その密度が97%以上であり、気孔をほとんど含まないような組織を持つようにするのが好ましい。

【0026】

【実施例】以下実施例を用いて本発明をさらに具体的に説明する。本発明で用いる圧電セラミックスとしては、一例として $Pb_{1-x}Sr_x(Mg_{1/3}Nb_{2/3})_A Ti_{1-x}Zr_xO_3$ 或いは、 $Pb(Ni_{1/3}Nb_{2/3})_A Ti_{1-x}Zr_xO_3$ 或いは $Pb(Ni_{1/3}Ta_{2/3})_A Ti_{1-x}Zr_xO_3$ (但し $A+B+C=1$) で示され、或いは $Pb_{1-x}Sr_x(Mg_{1/3}Nb_{2/3})_A(Ni_{1/3}Nb_{2/3})_B Ti_{1-x}Zr_xO_3$ または、 $Pb_{1-x}Sr_x(Mg_{1/3}Nb_{2/3})_A(Ni_{1/3}Ta_{2/3})_B Ti_{1-x}Zr_xO_3$ または $Pb(Ni_{1/3}Nb_{2/3})_A(Ni_{1/3}Ta_{2/3})_B Ti_{1-x}Zr_xO_3$ (但し $A+B+C+D=1$) で示され、これら材料系の焼結性を上げ、低温でも焼結でき、その微細構造を制御したような圧電セラミックス作製することとその製造方法を確立することを本発明の目的とする。その際、製造方法としては原料粉体の微粉碎を行うなどの方法がとられているが、その粉碎に 30 関して、有機溶剤を分散剤として混入して高濃度のスラリーを用いるのだが、スラリーの水素イオン濃度を大きく変えてしまうような原料粉を用いる場合そのスラリーの水素イオン濃度を調整して、スラリーのゲル化を防ぐことも重要である。

【0027】本発明の一例を示すと、圧電セラミックス粉末として組成が $Pb_{0.9}Sr_{0.1}(Mg_{1/3}Nb_{2/3})_A Ti_{1-x}Zr_xO_3$ 、及び $Pb(Ni_{1/3}Nb_{2/3})_A Ti_{1-x}Zr_xO_3$ など原料粉末を媒体攪拌ミルを用いて、直径0.6mmのジルコニア玉石と共に、有機系の分散剤及び水を加え、平均粒子径約0.2μmに粉碎したのち乾燥させ、造粒した。この粉体を、金型を用いて直径13mm、厚さ約1mmの円板状の成形体を作製し、通常の焼成温度よりも低温で2時間焼成し、微細構造を制御した圧電セラミックスを製造する。

【0028】なお以下の実施例においては、 ϵ ：誘電率、 ϵ_0 ：真空中の誘電率、 k_z ：径方向振動の電気機械結合係数、 d_{31} ：分極軸と垂直な方向の圧電定数をそれぞれ示す。

【0029】〈実施例1〉原料粉末として PbO 、 $SrCO_3$ 、 MgO 、 Nb_2O_5 、 TiO_2 、 ZrO_2 を用い、組成は第1表のようになるようにした。所定の組成に配合した混合粉体に純水及び分散剤を加えてスラリーとし、媒体攪拌ミルを用いて混合粉碎を行った。混合粉碎後の平均粒径はレーザ式粒子径測定器で測りながら、各組成とも0.2μm以下なるようにした。得られた混合粉を2時間仮焼した。さらに媒体攪拌ミルを用いて、直径0.6mmのジルコニア玉石と共に、有機系の分散剤及び水を加え、平均粒子径約0.4μm以下に粉碎した。比較例のため粉碎の進んでいない平均粒子径の異なる粉碎も行った。これを乾燥させ焼結前の原料粉末を得た。この粉末を有機バインダーと共にまぜ、500μmの篩を通過させて整粒した。この粉体を、金型を用いて直径13mm、厚さ約1mmの円板状の成形体を作製し、これを電気炉で2時間焼成し、圧電セラミックスを作製した。昇温・降温速度は300℃/hである。次に、各々試料の両面にCr-Auの蒸着電極を付与し、その後120℃のシリコンオイル中で両電極間に3kV/mmの直流電界を30分間印加して分極処理し、圧電素子を得た。この試料について、圧電特性を測定し、またSEM写真より微細構造の観察を行い結晶粒径の分布をインターセプト法によりもとめた。測定結果を(表1)に示す。

【0030】

〔表1〕

Pb _{1-x} Sr _x (Mg _{1/3} Nb _{2/3}) _{1-y} Ti _y Zr _{1-y} O ₃									
No.	x	A	B	C	平均粒径 μm	ε/ε ₀	k _p %	d ₃₁ × 10 ⁻¹⁰ m/V	平均粒径 μm
*1	0.1	0.255	0.4	0.345	0.37	4653	54.3	-2.25	2.5
*2	0.1	0.255	0.395	0.35	0.36	5042	57.8	-2.44	2.4
*3	0.1	0.255	0.39	0.355	0.33	5350	60.9	-2.85	2.9
*4	0.1	0.255	0.385	0.36	0.39	5470	65.7	-3.28	2.1
*5	0.1	0.255	0.38	0.365	0.37	5320	66.5	-3.27	2.5
*6	0.1	0.255	0.375	0.37	0.36	4570	66.2	-3.02	2.4
*7	0.1	0.255	0.37	0.375	0.37	3850	63.2	-2.35	2.5
*8	0.1	0.255	0.365	0.38	0.36	3160	60.6	-1.74	2.4
*9	0.05	0.255	0.38	0.365	0.33	1880	64.0	-2.32	2.9
*10	0.15	0.255	0.38	0.365	0.33	3300	65.5	-3.16	2.9
11	0.25	0.255	0.38	0.365	0.33	4890	65.2	-3.12	2.8
*12	0.1	0.255	0.38	0.365	0.22	5303	67.7	-3.53	1.5
*13	0.1	0.255	0.38	0.365	0.63	5218	66.6	-3.42	2.4
14	0.1	0.255	0.38	0.365	1.0	5342	63.3	-3.22	3.9
15	0.1	0.255	0.38	0.365	3.2	5071	59.9	-2.96	5.1

(備考) * は本発明の範囲内 (以下の表においても同じ)

【0031】(表1)から明らかなように、本発明の圧電セラミックスは、同一の組成のNo.12～No.14のいずれの圧電特性に関しても向上が見られる。本実施例では、平均粒径が0.4μm以下の微粉体を用いることにより、1200℃の低温で焼成でき、微細構造の制御したことによって、圧電セラミックスの特性が大きく向上している。また、平均粉末粒径が0.22μmのNo.12及び0.63μmのNo.13はその平均粒径の2倍以上の大きさの粉体の比率がそれぞれ3wt%、6wt%以上であり、No.14、No.15のはそれぞれ8wt%13wt%であった。即ち、比較例である粉体の粒度分布を平均粒径の2倍以上の大きさの粉体の比率が7wt%以上の微粉体から作製したNo.14、及びNo.15は、微細構造の制御できておらず、同時に微粉砕もしていないため、結晶粒径が5.1μmとなり、焼成温度も高く、特性も良くない。

【0032】(実施例2)原料粉末としてPbO、SrCO₃、MgO、Nb₂O₅、TiO₂、ZrO₂、Fe₂O₃を用い、組成は第2表のようになるようにした。所定の組成に配合した混合粉体に純水及び分散剤を加えてスラリーとし、媒体攪拌ミルを用いて混合粉砕を

行った。混合粉砕後の平均粒径はレーザ式粒子径測定器で測りながら、各組成とも0.2μm以下なるようにした。得られた混合粉を2時間仮焼した。さらに媒体攪拌ミルを用いて、直径0.6mmのジルコニア玉石と共に、有機系の分散剤及び水を加え、平均粒径約0.4μm以下に粉砕した。これを乾燥させ焼結前の原料粉末を得た。この粉末を有機バインダーと共にまぜ、500μmの篩を通過させて整粒した。この粉体を、金型を用いて直径13mm、厚さ約1mmの円板状の成形体を作製し、これを電気炉で2時間焼成し、圧電セラミックスを作製した。昇温・降温速度は300℃/hである。次に、各々試料の両面にCr-Auの蒸着電極を付与し、その後120℃のシリコンオイル中で両電極間に3kV/mmの直流電界を30分間印加して分極処理し、圧電素子を得た。この試料について、圧電特性を測定し、またSEM写真より微細構造の観察を行い結晶粒径の分布をインターセプト法によりもとめた。測定結果を(表2)に示す。

【0033】

【表2】

Pb _{0.9} Sr _{0.1} (Mg _{1/3} Nb _{2/3}) _A Ti ₈ ZrCO ₃₊₁ Fe ₂ O ₃									
No.	y	A	B	C	平均粒径 μm	ε/ε ₀	k _p %	d ₃₁ × 10 ⁻¹⁰ m/V	平均結晶径 μm
* 1	0	0.255	0.38	0.365	0.37	5130	63.7	-3.06	2.5
* 2	0.05	0.255	0.38	0.365	0.36	5420	64.9	-3.38	2.4
* 3	0.1	0.255	0.38	0.365	0.33	5360	65.2	-3.40	2.9
* 4	0.15	0.255	0.38	0.365	0.39	5270	64.7	-3.29	2.1
* 5	0.2	0.255	0.38	0.365	0.37	5120	62.5	-3.27	2.5
* 6	0.25	0.255	0.38	0.365	0.36	5050	61.5	-3.02	2.4
* 7	0.1	0.255	0.4	0.345	0.37	5150	58.2	-2.25	2.5
* 8	0.1	0.255	0.37	0.375	0.37	3850	61.7	-2.35	2.5
* 9	0.1	0.255	0.365	0.38	0.36	3160	59.6	-1.74	2.4

【0034】（表2）から明らかなように、本実施例のNo.2～No.9の圧電セラミックスは、単一の組成のNo.1よりも、圧電特性の向上が見られる。本実施例では、粒径分布の調整された平均粒子径が0.4 μm以下の微粉体を用いさらにFe₂O₃を添加することにより、1200℃の低温で焼成でき、微細構造を制御したことによって、圧電セラミックスの特性が大きく向上している。

【0035】（実施例3）原料粉末としてPbO, SrCO₃, MgO, Nb₂O₅, TiO₂, ZrO₂を用い、組成は第3表のようになるようにした。所定の組成に配合した混合粉体に純水及び分散剤を加えてスラリーとし、媒体攪拌ミルを用いて混合粉碎を行った。混合粉碎後の平均粒径はレーザ式粒子径測定器で測りながら、各組成とも0.2 μm以下なるようにした。得られた混合粉を2時間仮焼した。さらに媒体攪拌ミルを用いて、直径0.6 mmのジルコニア玉石と共に、有機系の分散剤

及び水を加え、平均粒子径約0.4 μm以下に粉碎した。比較例のため粉碎の進んでいない平均粒子径の異なる粉碎も行った。これを乾燥させ焼結前の原料粉末を得た。この粉末を有機バインダーと共にまぜ、500 μmの篩を通過させて整粒した。この粉体を、金型を用いて直径13 mm、厚さ約1 mmの円板状の成形体を作製し、これを電気炉で2時間焼成し、圧電セラミックスを作製した。昇温・降温速度は300℃/hである。次に、各々試料の両面にCr-Auの蒸着電極を付与し、その後120℃のシリコンオイル中で両電極間に3 kV/mmの直流電界を30分間印加して分極処理し、圧電素子を得た。この試料について、圧電特性を測定し、またSEM写真より微細構造の観察を行い結晶粒径の分布をインターセプト法によりもとめた。測定結果を（表3）に示す。

【0036】

【表3】

Pb _{1-x} Sr _x (Ni _{1/3} Nb _{2/3}) _{1-y} Ti _y Zr _{1-y} O ₃									
No.	x	A	B	C	平均粒径 μm	ε/ε ₀	k _p %	d ₃₁ × 10 ⁻¹⁰ m/V	平均粒径 μm
*1	0	0.4	0.38	0.22	0.35	4610	62.1	-3.08	2.7
*2	0	0.45	0.365	0.185	0.32	5510	57.1	-2.78	2.3
*3	0	0.45	0.360	0.190	0.35	5190	67.0	-3.53	2.0
*4	0	0.45	0.355	0.195	0.34	6200	63.4	-3.48	2.6
*5	0	0.45	0.350	0.200	0.35	5950	66.2	-3.66	2.0
6	0	0.45	0.350	0.200	3.2	5190	61.2	-3.03	5.5
*7	0	0.45	0.345	0.205	0.36	5680	59.7	-3.03	2.8
*8	0.02	0.45	0.375	0.37	0.36	4570	66.2	-3.02	2.4
*9	0.05	0.45	0.37	0.375	0.37	3850	63.2	-2.35	2.5
10	0.07	0.45	0.365	0.38	0.36	3160	60.6	-1.74	2.4
11	0	0.475	0.165	0.360	2.9	5120	55.6	-2.63	6.3
12	0	0.475	0.170	0.355	2.8	5410	57.8	-2.89	6.3
13	0	0.475	0.175	0.350	2.6	5710	60.2	-3.23	6.1
14	0	0.475	0.180	0.345	2.7	5480	63.7	-3.37	5.8
15	0	0.475	0.185	0.340	3.1	4560	63.7	-3.02	6.1
16	0	0.475	0.190	0.335	3.0	3850	60.2	-2.51	5.9
17	0	0.475	0.195	0.330	3.2	3330	56.5	-2.13	6.2
18	0	0.475	0.200	0.325	3.2	2780	55.2	-1.85	6.2
*19	0	0.475	0.180	0.345	0.22	6420	66.3	-3.82	2.8
*20	0	0.5	0.175	0.325	0.28	6820	64.3	-3.77	2.9

【0037】(表3)から明らかなように、本実施例の圧電セラミックスは、同一の組成のNo.1~No.5及びNo.7~No.9及びNo.19、20のいずれの圧電特性に関しても向上が見られる。本実施例では、粒径分布の調整された平均粒径が0.4 μm以下の微粉体を用いることにより、1200℃の低温で焼成でき、微細構造の制御したことによって、圧電セラミックスの特性が大きく向上している。微細構造の制御できていない比較例はいずれも微粉砕しておらず、結晶粒径が5 μm以上となり、焼成温度も高く、特性も良くない。

【0038】(実施例4)原料粉末としてPbO、SrCO₃、MgO、Nb₂O₅、TiO₂、ZrO₂を用い、組成は第4表のようになるようにした。所定の組成に配合した混合粉体に純水及び分散剤を加えてスラリーとし、媒体攪拌ミルを用いて混合粉砕を行った。混合粉砕後の平均粒径はレーザ式粒子径測定器で測りながら、各組成とも0.2 μm以下なるようにした。得られた混合

粉を2時間仮焼した。さらに媒体攪拌ミルを用いて、直径0.6 mmのジルコニア玉石と共に、有機系の分散剤及び水を加え、平均粒子径約0.4 μm以下に粉砕した。比較例のため粉砕の進んでいない平均粒子径の異なる粉砕も行った。これを乾燥させ焼結前の原料粉末を得た。この粉末を有機バインダーと共に混ぜ、500 μmの篩を通過させて整粒した。この粉体を、金型を用いて直径13 mm、厚さ約1 mmの円板状の成形体を作製し、これを電気炉で2時間焼成し、圧電セラミックスを作製した。昇温・降温速度は300℃/hである。次に、各々試料の両面にCr-Auの蒸着電極を付与し、その後120℃のシリコンオイル中で両電極間に3 kV/mmの直流電界を30分間印加して分極処理し、圧電素子を得た。この試料について、圧電特性を測定し、またSEM写真より微細構造の観察を行い結晶粒径の分布をインターセプト法によりもとめた。測定結果を(表4)に示す。

【0039】

【表4】

Pb (Ni _{1/3} Ta _{1/3}) _A Ti _B Zr _C O ₃									
No.	x	A	B	C	平均粒径 μm	ε/ε ₀	k _p %	d ₃₁ × 10 ⁻¹⁰ m/V	平均粒径 μm
*1	0	0.450	0.350	0.200	3.3	9700	24.7	-1.34	6.4
*2	0	0.400	0.382	0.218	3.5	5520	55.7	-3.16	6.3
*3	0	0.375	0.398	0.227	3.5	4530	54.9	-3.04	6.7
*4	0	0.350	0.414	0.236	3.4	3540	54.5	-2.16	6.1
*5	0	0.300	0.445	0.255	3.6	1960	44.7	-1.09	6.2
*6	0	0.380	0.405	0.215	3.4	5890	52.3	-2.45	6.5
*7	0	0.380	0.400	0.220	3.6	6740	52.6	-2.85	6.4
*8	0	0.380	0.395	0.225	3.9	6520	55.8	-2.94	6.2
*9	0	0.380	0.390	0.230	3.5	6190	53.8	-2.86	6.4
*10	0	0.380	0.385	0.235	3.8	4420	46.0	-2.74	6.3
*11	0	0.450	0.350	0.200	0.35	9700	27.6	-1.59	2.8
*12	0	0.400	0.382	0.218	0.32	6010	57.8	-3.41	2.3
*13	0	0.375	0.398	0.227	0.35	5190	59.2	-3.29	2.6
*14	0	0.350	0.414	0.236	0.34	4150	55.7	-2.42	2.8
*15	0	0.300	0.445	0.255	0.35	2460	47.7	-1.36	2.4
*16	0	0.380	0.405	0.215	0.32	6600	53.9	-2.75	2.9
*17	0	0.380	0.400	0.220	0.36	7340	56.9	-3.10	2.3
*18	0	0.380	0.395	0.225	0.36	7110	58.3	-3.23	2.5
*19	0	0.380	0.390	0.230	0.37	6830	58.0	-3.15	2.6
*20	0	0.380	0.385	0.235	0.36	4980	50.6	-2.20	2.4

【0040】(表4)から明らかなように、本実施例のNo.10～No.20の圧電セラミックスは、いずれの同一組成のNo.1～No.10の圧電セラミックスと比較して圧電特性の向上が見られる。本実施例では、粒径分布の調整された平均粒径が0.4 μm以下の微粉体を用いることにより、低温で焼成でき、微細構造を制御したことによ

って、圧電セラミックスの特性が大きく向上している。
【0041】(実施例5)原料粉末としてPbO, SrCO₃, MgO, Nb₂O₅, TiO₂, ZrO₂を用い、組成は第5表のようにした。所定の組成に配合した混合粉体に純水及び分散剤を加えてスラリーとし、媒体攪拌ミルを用いて混合粉碎を行った。混合粉碎後の平均粒径はレーザ式粒子径測定器で測りながら、各組成とも0.2 μm以下なるようにした。得られた混合粉を2時間仮焼した。さらに媒体攪拌ミルを用いて、直

径0.6 mmのジルコニア玉石と共に、有機系の分散剤及び水を加え、平均粒径約0.4 μm以下に粉碎した。比較例のため粉碎の進んでいない平均粒径の異なる粉碎も行った。これを乾燥させ焼結前の原料粉末を得た。この粉末を有機バインダーと共にまぜ、500 μmの篩を通過させて整粒した。この粉体を、金型を用いて直径13 mm、厚さ約1 mmの円板状の成形体を作製し、これを電気炉で2時間焼成し、圧電セラミックスを作製した。昇温・降温速度は300℃/hである。次に、各々試料の両面にCr-Auの蒸着電極を付与し、その後120℃のシリコンオイル中で両電極間に3 kV/mmの直流電界を30分間印加して分極処理し、圧電素子を得た。この試料について、圧電特性を測定し、またSEM写真より微細構造の観察を行い結晶粒径の分布をインターセプト法によりもとめた。測定結果を(表5)に示す。

【0042】

【表5】

Pb _{1-x} Sr _x (Mg _{1/3} Nb _{2/3}) _A (Ni _{1/3} Nb _{2/3}) _B Ti _C Zr _D O ₃										
No.	x	A	B	C	D	平均粒径 μm	c/e ₀	k _p %	d ₃₁ ×10 ⁻¹⁰ m/V	平均焼成温度 μm
#1	0.02	0.05	0.35	0.35	0.25	0.35	5210	64.1	-3.45	2.7
#2	0.04	0.10	0.21	0.35	0.34	0.32	5550	64.6	-3.53	2.3
#3	0.06	0.15	0.14	0.36	0.35	0.35	5860	65.5	-3.58	2.0
#4	0.08	0.20	0.07	0.36	0.37	0.34	5970	66.4	-3.60	2.6
Pb _{1-x} Sr _x (Mg _{1/3} Nb _{2/3}) _A (Ni _{1/3} Ta _{2/3}) _B Ti _C Zr _D O ₃										
#5	0.02	0.05	0.35	0.38	0.21	0.35	5880	60.8	-3.32	2.7
#6	0.04	0.10	0.21	0.38	0.31	0.32	5510	62.5	-3.28	2.5
#7	0.06	0.15	0.14	0.38	0.33	0.35	5350	63.0	-3.23	2.6
#8	0.08	0.20	0.07	0.38	0.35	0.34	5140	63.4	-3.11	2.9
Pb _{1-x} Sr _x (Ni _{1/3} Nb _{2/3}) _A (Ni _{1/3} Ta _{2/3}) _B Ti _C Zr _D O ₃										
#9	0	0.05	0.35	0.35	0.30	0.35	6510	59.4	-3.61	2.3
#10	0	0.10	0.21	0.35	0.34	0.32	6210	61.7	-3.58	2.4
#11	0	0.15	0.14	0.35	0.36	0.35	5990	62.9	-3.56	2.3
#12	0	0.20	0.07	0.36	0.37	0.34	5700	63.6	-3.55	2.7

【0043】（表5）から本実施例では、粒径分布の調整された平均粒子径が0.4 μm以下の微粉体を用いることにより、低温で焼成でき、微細構造を制御したことによって、従来の特性よりその特性が大きく向上している。

【0044】

【発明の効果】以上のように、本発明の圧電セラミックスでは、媒体攪拌ミルによる微粉砕により焼成温度を低下させ微細構造を制御することにより、圧電セラミックスの圧電特性を向上させることができる。

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(54) PIEZOELECTRIC ELEMENT MATERIAL AND ITS PRODUCTION

(57) Abstract:

PURPOSE: To enable sintering even at a low temp. by using Pb-contg. ceramics having a specified average grain size and a specified grain size distribution and to obtain a piezoelectric element material having improved piezoelectric characteristics of piezoelectric ceramics by controlling the fine structure of the Pb-contg. ceramics.

CONSTITUTION: This piezoelectric element material contains Pb-contg. ceramics having 0.5-5[μ]m average grain size and a grain size distribution in which [ge]90wt.% grains are within the range of 0.5-5[μ]m. The basic compsn. of this material is preferably represented by the general formula $Pb_{1-x}Sr_x(Mg_{1/3}Nb_{2/3}aTibZrcO_3$ (where $a+b+c=1$, $0.20 \leq a \leq 0.30$, $0.30 \leq b \leq 0.45$, $0.30 \leq c \leq 0.40$ and $0.01 \leq x \leq 0.20$) and 0.01-0.2wt.% Fe₂O₃ is preferably added to the basic compsn.

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 CLAIMS

[Claim(s)]

[Claim 1] The piezoelectric-device ingredient containing Pb system ceramics which the diameter of average crystal grain of the ceramics is 0.5-5 micrometers, and is distributed while the particle of said mean particle diameter is 0.5-5 micrometers 90 % of the weight or more.

[Claim 2] The piezoelectric-device ingredient containing Pb system ceramics which the diameter of average crystal grain is 1-3 micrometers, and is distributed while the particle of said diameter of average crystal grain is 1-3 micrometers 75 % of the weight or more according to claim 1.

[Claim 3] A piezoelectric-device ingredient presentation is general formula $Pb_{1-x} Sr_x A TiB ZrC O (Mg_{1/3} Nb_{2/3})_3$. It is shown (however, $A+B+C=1$), The piezoelectric-device ingredient according to claim 1 or 2 which uses as a principal component the basic presentation with which are satisfied of $0.20 \leq A \leq 0.30$, $0.30 \leq B \leq 0.45$, $0.30 \leq C \leq 0.40$, $0.01 \leq x \leq 0.20$.

[Claim 4] Fe_2O_3 0.01 - 0.2% of the weight of piezoelectric-device ingredient according to claim 3 which recognizes range existence.

[Claim 5] A presentation is general formula $Pb(nickel_{1/3} Nb_{2/3}) A TiB ZrC O_3$. It is shown (however, $A+B+C=1$),

The piezoelectric-device ingredient according to claim 1 which uses as a principal component the basic presentation with which are satisfied of $0.40 \leq A \leq 0.55$, $0.15 \leq B \leq 0.30$, $0.10 \leq C \leq 0.30$.

[Claim 6] Fe_2O_3 0.01 - 0.5% of the weight of piezoelectric-device ingredient according to claim 5 which recognizes range existence.

[Claim 7] A presentation is general formula $Pb_{1-x} Sr_x A TiB ZrC O (nickel_{1/3} Nb_{2/3})_3$. It is shown (however, $A+B+C=1$),

The piezoelectric-device ingredient according to claim 1 or 2 which uses as a principal component the basic presentation with which are satisfied of $0.35 \leq A \leq 0.55$, $0.15 \leq B \leq 0.40$, $0.15 \leq C \leq 0.40$, $0.01 \leq x \leq 0.10$.

[Claim 8] Fe_2O_3 0.01 - 0.5% of the weight of piezoelectric-device ingredient according to claim 5 which recognizes range existence.

[Claim 9] General formula $Pb(nickel_{1/3} Ta_{2/3}) B TiC ZrD O_3$ It is shown (however, $A+B+C=1$),

at least one sort of metals chosen from alkaline earth metal and rare earth elements in a part of Pb to the piezoelectric-device ingredient which uses as a principal component the basic presentation with which are satisfied of $0.25 \leq A \leq 0.45$, $0.20 \leq B \leq 0.35$, $0.20 \leq C \leq 0.40$ -- 0.01-0.2-mol % -- permuting -- and -- as an accessory constituent -- Fe_2O_3 Piezoelectric-device ingredient according to claim 1 or 2 whose 0.01 - 0.5 % of the weight was made to exist.

[Claim 10] A presentation General formula $Pb_{1-x} Sr_x A (Mg_{1/3} Nb_{2/3}) B TiC ZrD O (nickel_{1/3} Nb_{2/3})_3$ Or $Pb_{1-x} Sr_x A (Mg_{1/3} Nb_{2/3}) B TiC ZrD O_3 (nickel_{1/3} Ta_{2/3})$ Or $Pb(nickel_{1/3} Nb_{2/3}) A B TiC ZrD O_3 (nickel_{1/3} Ta_{2/3})$ It is shown. (However, $A+B+C+D=1$)

They are 0.01 - 0.5 % of the weight, and Fe_2O_3 as an accessory constituent to the piezoelectric-device ingredient which uses as a principal component the basic presentation with which are satisfied of

$0.05 \leq A \leq 0.55$, $0.05 \leq B \leq 0.55$, $0.15 \leq C \leq 0.30$, $0.15 \leq D \leq 0.30$, $0.01 \leq x \leq 0.20$ about at least one sort chosen from the oxide of rare earth elements. Piezoelectric-device ingredient according to claim 1 or 2 which comes to carry out addition content 0.05 to 0.5% of the weight.

[Claim 11] The pulverized coal in which the mean particle diameter of fine particles is 0.4 micrometers or less, and the particle size distribution of said fine particles contain the rate of a particle twice [more than] the magnitude of said mean particle diameter 7% of the weight or more is used as charge fine particles of sintering Maebaru. The manufacture approach of a piezoelectric-device ingredient that the diameter of average crystal grain of the

ceramics obtains the piezoelectric-device ingredient containing Pb system ceramics distributed while the particle of 0.5-5 micrometers and said mean particle diameter is 0.5-5 micrometers 90 % of the weight or more by sintering the charge fine particles of sintering Maebaru.

[Claim 12]The manufacture approach of the piezoelectric-device ingredient according to claim 11 the volume of a fine-particles medium is a 4 or less times [of the true volume of fine particles] amount, add and grind a dispersant, and using the minute ball 0.6mm or less.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to piezoelectric-device ingredients, such as electrostrictive ceramics, electrostriction ceramics, etc. which are used for applications, such as pyroelectric elements, such as piezoelectric devices, such as positioning of a precision instrument, an electrostrictive actuator for video auto tracking, a ceramic filter, and a ceramic radiator, an infrared sensor, and an linear array sensor.

[0002]

[Description of the Prior Art]As the ferroelectricity ceramics or electrostrictive ceramics, it is Pb(Ti, Zr) O₃ from the former. Binary system and Pb(Mg¹ / 3 Nb^{2/3}) xTi_y ZrO₃ Three-component system and Pb(Zn¹ / 3 Nb^{2/3}) A B TiCZrD₃ (Sn¹ / 3 Nb^{2/3}) There is a ceramic ingredient which consists of a quaternary system presentation etc. After all are almost ceramics and the constituent fabricates a raw material or temporary-quenching powder in a predetermined configuration, it calcinates these conventional ceramic ingredients at an elevated temperature, and they are produced. In the electrostrictive ceramics of these former, by choosing the presentation ratio of a component, the electrostrictive ceramics of various properties is produced according to an application, and it is used for the application of an actuator, a ceramic filter, a piezo-electric buzzer, a piezo-electric ignition plug, an ultrasonic vibrator, etc.

[0003]

[Problem(s) to be Solved by the Invention]Neither the evaporation on [PbO] the production nor generation of a secondary phase escaped the conventional electrostrictive ceramics, and the ceramics in which the property which the ingredient system has enough is shown was not obtained. It was difficult to demonstrate enough the property which a sufficiently precise sintered compact is not obtained when alkaline earth elements, such as an element, for example, Sr etc., which checks especially a degree of sintering, are included, but the ingredient has. Then, it is the need to raise the degree of sintering and to control detailed structure, in order to obtain the ceramics with the outstanding property.

[0004]In order that this invention may solve said conventional problem, it can be sintered also at low temperature and aims at offering the piezoelectric-device ingredient which controlled the fine structure and improved the piezo-electric property of electrostrictive ceramics, and its manufacture approach.

[0005]

[Means for Solving the Problem]In order to attain said purpose, the piezoelectric-device ingredient of this invention is equipped with the configuration that Pb system ceramics with which the diameter of average crystal grain of the ceramics is 0.5-5 micrometers, and the particle of said mean particle diameter is distributed 90 % of the weight or more while being 0.5-5 micrometers is included.

[0006] In said configuration, it is desirable that Pb system ceramics which the diameter of average crystal grain is 1-3 micrometers, and is distributed while the particle of said diameter of average crystal grain is 1-3 micrometers 75 % of the weight or more is included.

[0007] Moreover, it sets in said configuration and a piezoelectric-device ingredient presentation is general formula $Pb_{1-x} Sr_x A TiB ZrC O (Mg_{1/3} Nb_{2/3})_3$. It is shown (however, $A+B+C=1$), It is desirable to use as a principal component the basic presentation with which are satisfied of $0.20 \leq A \leq 0.30$, $0.30 \leq B \leq 0.45$, $0.30 \leq C \leq 0.40$, $0.01 \leq x \leq 0.20$.

[0008] Moreover, it sets in said configuration and is Fe 2O₃. 0.01 - 0.2% of the weight of the thing for which range existence is recognized is desirable. Moreover, it sets in said configuration and a presentation is general formula $Pb(nickell / 3 Nb_{2/3}) A TiB ZrC O_3$. It is shown (however, $A+B+C=1$), It is desirable to use as a principal component the basic presentation with which are satisfied of $0.40 \leq A \leq 0.55$, $0.15 \leq B \leq 0.30$, $0.10 \leq C \leq 0.30$.

[0009] Moreover, it sets in said configuration and is Fe 2O₃. 0.01 - 0.5% of the weight of the thing for which range existence is recognized is desirable. Moreover, it sets in said configuration and a presentation is general formula $Pb_{1-x} Sr_x A TiB ZrC O (nickell / 3 Nb_{2/3})_3$. It is shown (however, $A+B+C=1$),

It is desirable to use as a principal component the basic presentation with which are satisfied of $0.35 \leq A \leq 0.55$, $0.15 \leq B \leq 0.40$, $0.15 \leq C \leq 0.40$, $0.01 \leq x \leq 0.10$.

[0010] Moreover, it sets in said configuration and is Fe 2O₃. 0.01 - 0.5% of the weight of the thing for which range existence is recognized is desirable. Moreover, it sets in said configuration and is general formula $Pb(nickell / 3 Ta_{2/3}) B TiC ZrD O_3$. It is shown (however, $A+B+C=1$), at least one sort of metals chosen from alkaline earth metal and rare earth elements in a part of Pb to the piezoelectric-device ingredient which uses as a principal component the basic presentation with which are satisfied of $0.25 \leq A \leq 0.45$, $0.20 \leq B \leq 0.35$, $0.20 \leq C \leq 0.40$ -- 0.01-0.2-mol % -- permuting -- and -- as an accessory constituent -- Fe 2O₃ It is desirable to make 0.01 - 0.5 % of the weight exist.

[0011] In said configuration a presentation Moreover, general formula $Pb_{1-x} Sr_x A (Mg_{1/3} Nb_{2/3}) B TiC ZrD O (nickell / 3 Nb_{2/3})_3$ Or $Pb_{1-x} Sr_x A (Mg_{1/3} Nb_{2/3}) B TiC ZrD O_3 (nickell / 3 Ta_{2/3})$ Or $Pb(nickell / 3 Nb_{2/3}) A B TiC ZrD O_3 (nickell / 3 Ta_{2/3})$ It is shown. (However, $A+B+C+D=1$)

They are 0.01 - 0.5 % of the weight, and Fe 2O₃ as an accessory constituent to the piezoelectric-device ingredient which uses as a principal component the basic presentation with which are satisfied of $0.05 \leq A \leq 0.55$, $0.05 \leq B \leq 0.55$, $0.15 \leq C \leq 0.30$, $0.15 \leq D \leq 0.30$, $0.01 \leq x \leq 0.20$ about at least one sort chosen from the oxide of rare earth elements. It is desirable to come to carry out addition content 0.05 to 0.5% of the weight.

[0012] Next, the mean particle diameter of fine particles of the manufacture approach of the piezoelectric-device ingredient of this invention is 0.4 micrometers or less. And the pulverized coal in which the particle size distribution of said fine particles contain the rate of a particle twice [more than] the magnitude of said mean particle diameter 7% of the weight or more is used as charge fine particles of sintering Maebaru. The charge fine particles of sintering Maebaru are sintered, and the diameter of average crystal grain of the ceramics is equipped with the configuration that the particle of 0.5-5 micrometers and said mean particle diameter obtains the piezoelectric-device ingredient containing Pb system ceramics distributed 90 % of the weight or more while being 0.5-5 micrometers.

[0013] It is desirable to have set in said configuration, for the volume of a fine-particles medium to be a 4 or less times [of the true volume of fine particles] amount, to have added and ground the dispersant, and to have used the minute ball 0.6mm or less.

[0014]

[Function] According to the configuration of the piezoelectric-device ingredient of said this invention, by including Pb system ceramics which the diameter of average crystal grain of the ceramics is 0.5-5 micrometers, and is distributed while the particle of said mean particle diameter is 0.5-5 micrometers 90 % of the weight or more, the piezo-electric property of electrostrictive ceramics, for example, the absolute value of a piezoelectric constant d_{31} , is large, and electrostrictive ceramics also with the large value of other piezoelectric constants d_{33} and d_{15} can be obtained.

[0015] According to the desirable configuration that Pb system ceramics which the diameter of average crystal grain is 1-3 micrometers, and is distributed in the above while the particle of said diameter of average crystal grain is 1-3 micrometers 75 % of the weight or more is included. When it is the ceramics with the precise magnitude of the pore which exists in the grain boundary section, depending on the crystal particle diameter, it can become sufficiently small, or the number can also decrease very much, and the property which an ingredient has can fully be demonstrated.

[0016] Moreover, it sets above and a piezoelectric-device ingredient presentation is general formula $Pb_{1-x}Sr_xA TiB ZrC O (Mg_{1/3} Nb_{2/3})_3$. It is shown (however, $A+B+C=1$),

According to the desirable configuration of using as a principal component the basic presentation with which are satisfied of $0.20 \leq A \leq 0.30$, $0.30 \leq B \leq 0.45$, $0.30 \leq C \leq 0.40$, $0.01 \leq x \leq 0.20$, it is a mol photograph pick. Phase It becomes the presentation near a boundary and they are specific-inductive-capacity ϵ_{nr} and an electromechanical coupling coefficient k_p . And k_{31} is large and can obtain an ingredient with the big absolute value of a piezoelectric constant d_{31} .

[0017] Moreover, it sets above and is Fe $2O_3$. According to 0.01 - 0.2% of the weight of the desirable configuration of recognizing range existence, the precise ceramics is obtained with crystal particle diameter more detailed than the part to which burning temperature falls, and an ingredient with the big absolute value of a piezoelectric constant can be obtained.

[0018] Moreover, it sets in said configuration and a presentation is general formula $Pb(nickel_{1/3} Nb_{2/3}) A TiB ZrC O_3$. It is shown (however, $A+B+C=1$),

According to the desirable configuration of using as a principal component the basic presentation with which are satisfied of $0.40 \leq A \leq 0.55$, $0.15 \leq B \leq 0.30$, $0.10 \leq C \leq 0.30$, it is a mol photograph pick. Phase It becomes the presentation near a boundary and they are specific-inductive-capacity ϵ_{nr} and an electromechanical coupling coefficient k_p . And k_{31} is large and can obtain an ingredient with the big absolute value of a piezoelectric constant d_{31} .

[0019] Moreover, it sets above and is Fe $2O_3$. According to 0.01 - 0.5% of the weight of the desirable configuration of recognizing range existence, the precise ceramics is obtained with crystal particle diameter more detailed than the part to which burning temperature falls, and an ingredient with the big absolute value of a piezoelectric constant can be obtained.

[0020] Moreover, it sets in said configuration and a presentation is general formula $Pb_{1-x}Sr_xATiB ZrC O (nickel_{1/3} Nb_{2/3})_3$. It is shown (however, $A+B+C=1$),

The value of the part specific inductive capacity in which the Curie point falls according to the desirable configuration of using as a principal component the basic presentation with which are satisfied of $0.35 \leq A \leq 0.55$, $0.15 \leq B \leq 0.40$, $0.15 \leq C \leq 0.40$, $0.01 \leq x \leq 0.10$ becomes large, and it is a mol photograph pick phase. It becomes the presentation near a boundary and an ingredient with the big absolute value of a piezoelectric constant d_{31} can be obtained.

[0021] Moreover, it sets above and is Fe $2O_3$. According to 0.01 - 0.5% of the weight of the desirable configuration of recognizing range existence, the precise

ceramics is obtained with crystal particle diameter more detailed than the part to which burning temperature falls, and an ingredient with the big absolute value of a piezoelectric constant can be obtained.

[0022] Moreover, it sets above and is general formula $Pb(nickell / 3 Ta 2/3) B TiC ZrD O3$. It is shown (however, $A+B+C=1$),

As opposed to the piezoelectric-device ingredient which uses as a principal component the basic presentation with which are satisfied of $0.25 \leq A \leq 0.45$, $0.20 \leq B \leq 0.35$, $0.20 \leq C \leq 0.40$ It permutes. at least one sort of metals chosen from alkaline earth metal and rare earth elements in a part of Pb -- 0.01-0.2-mol % -- as an accessory constituent Fe 2O3 According to the desirable configuration of making 0.01 - 0.5 % of the weight exist Mol photograph pick It becomes the presentation near a phase boundary and they are specific-inductive-capacity ϵ and an electromechanical coupling coefficient k_p . And k_{31} is large and can obtain an ingredient with the big absolute value of a piezoelectric constant d_{31} .

[0023] In the above a presentation Moreover, general formula $Pb_{1-x} Sr_x A (Mg_{1/3} Nb 2/3) B TiC ZrD O (nickell / 3 Nb 2/3) 3$ Or $Pb_{1-x} Sr_x A (Mg_{1/3} Nb 2/3) B TiC ZrD O3 (nickell / 3 Ta 2/3) Or Pb(nickell / 3 Nb 2/3) A B TiC ZrD O3 (nickell / 3 Ta 2/3)$ It is shown. (However, $A+B+C+D=1$)

As opposed to the piezoelectric-device ingredient which uses as a principal component the basic presentation with which are satisfied of $0.05 \leq A \leq 0.55$, $0.05 \leq B \leq 0.55$, $0.15 \leq C \leq 0.30$, $0.15 \leq D \leq 0.30$, $0.01 \leq x \leq 0.20$ As an accessory constituent, they are 0.01 - 0.5 % of the weight, and Fe 2O3 about at least one sort chosen from the oxide of rare earth elements. According to the desirable configuration of coming to carry out addition content 0.05 to 0.5% of the weight, an ingredient with the big absolute value of a piezoelectric constant d_{31} can be obtained like the above.

[0024] According to the configuration of the manufacture approach of the piezoelectric-device ingredient of this invention, the mean particle diameter of fine particles next, by 0.4 micrometers or less And the pulverized coal in which the particle size distribution of said fine particles contain the rate of a particle twice [more than] the magnitude of said mean particle diameter 7% of the weight or more is used as charge fine particles of sintering Maebaru. The diameter of average crystal grain of the ceramics by sintering the charge fine particles of sintering Maebaru by obtaining the piezoelectric-device ingredient containing Pb system ceramics distributed while the particle of 0.5-5 micrometers and said mean particle diameter is 0.5-5 micrometers 90 % of the weight or more The piezoelectric-device ingredient of said this invention can be manufactured rationally efficiently.

[0025] Though it is a high concentration medium, since a fluidity is a good medium according to the desirable configuration of having set above, the volume of a fine-particles medium being a 4 or less times [of the true volume of fine particles] amount, having added and ground the dispersant, and having used the minute ball 0.6mm or less, it excels in homogeneity and the minute ball is used, contact surface area also increases and it can pulverize to a difficult particle size in the usual grinding time amount. Moreover, the diameter of average crystal grain of electrostrictive ceramics is 1-5 micrometers or less, and it is desirable to make it consist of a uniform organization. Moreover, the consistency is 97% or more, and it is desirable to have the organization which hardly contains pore.

[0026]

[Example] This invention is explained still more concretely using an example below. as the electrostrictive ceramics used by this invention -- as an example -- $Pb_{1-x} Sr_x A TiB ZrC O (Mg_{1/3} Nb 2/3) 3$ Or $Pb(nickell / 3 Nb 2/3) A Ti-B ZrC O3$ Or it is shown by $Pb(nickell / 3 Ta 2/3) A TiB ZrC O3$ (however, $A+B+C=1$). Or $Pb_{1-x} Sr_x A (Mg_{1/3} Nb 2/3) B TiC ZrD O (nickell / 3 Nb 2/3) 3$ Or $Pb_{1-x} Sr_x A (Mg_{1/3} Nb 2/3) (nickell / 3 Ta 2/3) B TiC ZrD O3$ Or it is shown by $Pb(nickell / 3 Nb 2/3) A B TiC ZrD O (nickell / 3 Ta 2/3) 3$ (however, $A+B+C+D=1$). The degree of sintering of these ingredients system is raised, and it can sinter also at low

temperature, and sets it as the purpose of this invention to establish a thing [a thing] controlled the fine structure and which carries out electrostrictive ceramics production, and its manufacture approach. Although an organic solvent is mixed as a dispersant about the grinding although approaches, such as pulverizing raw material fine particles as the manufacture approach, are taken in that case, and a high-concentration slurry is used, it is also important to adjust the hydrogen ion concentration of the slurry, when using raw material powder into which the hydrogen ion concentration of a slurry is changed a lot, and to prevent gelation of a slurry.

[0027] When an example of this invention is shown, a presentation as electrostrictive ceramics powder $\text{Pb}_{0.9}\text{Sr}_{0.1}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.255}\text{Ti}_{0.38}\text{Zr}_{0.365}$, and $\text{Pb}(\text{nickel}_{1/3}\text{Nb}_{2/3})_{0.45}\text{Ti}_{0.35}\text{Zr}_{0.203}$ etc. -- after adding the dispersant and water of an organic system and grinding raw material powder in mean particle diameter of about 0.2 micrometers with a zirconia ball with a diameter of 0.6mm using a medium stirrer mill, it was made to dry, and it corned. A disc-like Plastic solid with a diameter [of 13mm] and a thickness of about 1mm is produced for these fine particles using metal mold, it calcinates at low temperature rather than the usual burning temperature for 2 hours, and the electrostrictive ceramics which controlled the fine structure is manufactured.

[0028] In addition, it sets in the following examples and is epsilon:dielectric constant and epsilon 0. : The dielectric constant in a vacuum, k_p : The electromechanical coupling coefficient of the direction vibration of a path and the piezoelectric constant of a direction perpendicular to a d_{31} :minute polar axis are shown, respectively.

[0029] (Example 1) They are PbO , SrCO_3 , MgO , Nb_2O_5 , TiO_2 , and ZrO_2 as raw material powder. It uses and was made for a presentation to become as for it to be shown in the 1st table. Pure water and a dispersant were added to the mixed fine particles blended with the predetermined presentation, it considered as the slurry, and preferential grinding was performed using the medium stirrer mill. Each presentation is 0.2, measuring the mean particle diameter after preferential grinding with a laser type particle diameter measuring instrument. It was made to become below. Temporary quenching of the obtained mixed powder was carried out for 2 hours. Furthermore, using the medium stirrer mill, with the zirconia ball with a diameter of 0.6mm, the dispersant and water of an organic system were added and it ground in mean particle diameter of about 0.4 micrometers or less. Grinding from which the mean particle diameter to which grinding is not progressing for the example of a comparison differs was also performed. This was dried and the raw material powder before sintering was obtained. This powder was mixed with the organic binder, the 500-micrometer screen was passed, and the particle size regulation was carried out. The disc-like Plastic solid with a diameter [of 13mm] and a thickness of about 1mm was produced for these fine particles using metal mold, this was calcinated with the electric furnace for 2 hours, and electrostrictive ceramics was produced. A temperature up and a temperature fall rate are 300 degrees C/h. Next, the vacuum evaporations electrode of Cr-Au is respectively given to both sides of a sample, and it is 3kV/mm between two electrodes in a 120-degree C silicone oil after that. Direct-current electric field were impressed for 30 minutes, polarization processing was carried out and the piezoelectric device was obtained. About this sample, the piezo-electric property was measured, and the fine structure was observed from the SEM photograph, and distribution of the diameter of crystal grain was searched for by the intercepting method. A measurement result is shown in (Table 1).

[0030]

(Table 1)

Pb _{1-x} Sr _x (Mg _{1/3} Nb _{2/3}) _{1-y} Ti _y Zr _{1-y} O ₃									
No.	x	A	B	C	平均粒径 μm	ε/ε ₀	k _p %	d ₃₁ × 10 ⁻¹⁰ m/V	平均粒径 μm
* 1	0.1	0.255	0.4	0.345	0.37	4653	54.3	-2.25	2.5
* 2	0.1	0.255	0.395	0.35	0.36	5042	57.8	-2.44	2.4
* 3	0.1	0.255	0.39	0.355	0.33	5350	60.9	-2.85	2.9
* 4	0.1	0.255	0.385	0.36	0.39	5470	65.7	-3.28	2.1
* 5	0.1	0.255	0.38	0.365	0.37	5320	66.5	-3.27	2.5
* 6	0.1	0.255	0.375	0.37	0.36	4570	66.2	-3.02	2.4
* 7	0.1	0.255	0.37	0.375	0.37	3850	63.2	-2.35	2.5
* 8	0.1	0.255	0.365	0.38	0.36	3160	60.6	-1.74	2.4
* 9	0.05	0.255	0.38	0.365	0.33	1880	64.0	-2.32	2.9
*10	0.15	0.255	0.38	0.365	0.33	3300	65.5	-3.16	2.9
11	0.25	0.255	0.38	0.365	0.33	4890	65.2	-3.12	2.8
*12	0.1	0.255	0.38	0.365	0.22	5303	67.7	-3.53	1.5
*13	0.1	0.255	0.38	0.365	0.63	5218	66.6	-3.42	2.4
14	0.1	0.255	0.38	0.365	1.0	5342	63.3	-3.22	3.9
15	0.1	0.255	0.38	0.365	3.2	5071	59.9	-2.96	5.1

(備考) * は本発明の範囲内 (以下の表においても同じ)

[0031] The electrostrictive ceramics of this invention is No.12 -No.14 of the same presentation so that clearly from (Table 1). Improvement is found also about which piezo-electric property. In this example, when mean particle diameter uses pulverized coal 0.4 micrometers or less, it can calcinate at 1200-degree C low temperature, and when the fine structure controlled, the property of electrostrictive ceramics is improving greatly. Moreover, average powder particle size is 0.22 micrometers. No.12 And 0.63 micrometers No.13 The ratios of fine particles twice [more than] the magnitude of the mean particle diameter are 3wt(s)% and more than 6wt%, respectively, and it is No.14 and No.15. That was 8wt%13wt%, respectively. Namely, No.14 to which the ratio of fine particles twice [more than] the magnitude of mean particle diameter produced the particle size distribution of the fine particles which are the examples of a comparison from the pulverized coal beyond 7wt% and No.15 Since the fine structure cannot be controlled and pulverizing has not been carried out to coincidence, either, the diameter of crystal grain is set to 5.1 micrometers, burning temperature is also high, and a property is not good, either.

[0032] (Example 2) They are PbO, SrCO₃, MgO, Nb₂O₅, TiO₂, ZrO₂, and Fe₂O₃ as raw material powder. It uses and was made for a presentation to become as for it to be shown in the 2nd table. Pure water and a dispersant were added to the mixed fine particles blended with the predetermined presentation, it considered as the slurry, and preferential grinding was performed using the medium stirrer mill. Each presentation is 0.2, measuring the mean particle diameter after preferential grinding with a laser type particle diameter measuring instrument. μm It was made to become below. Temporary quenching of the obtained mixed powder was carried out for 2 hours. Furthermore, using the medium stirrer mill, with the zirconia ball with a diameter of 0.6mm, the dispersant and water of an organic system were added and it ground in mean particle diameter of about 0.4

micrometers or less. This was dried and the raw material powder before sintering was obtained. This powder was mixed with the organic binder, the 500-micrometer screen was passed, and the particle size regulation was carried out. The disc-like Plastic solid with a diameter [of 13mm] and a thickness of about 1mm was produced for these fine particles using metal mold, this was calcinated with the electric furnace for 2 hours, and electrostrictive ceramics was produced. A temperature up and a temperature fall rate are 300 degrees C/h. Next, the vacuum evaporatio electrode of Cr-Au is respectively given to both sides of a sample, and it is 3kV/mm between two electrodes in a 120-degree C silicone oil after that. Direct-current electric field were impressed for 30 minutes, polarization processing was carried out and the piezoelectric device was obtained. About this sample, the piezo-electric property was measured, and the fine structure was observed from the SEM photograph, and distribution of the diameter of crystal grain was searched for by the intercepting method. A measurement result is shown in (Table 2).

[0033]

[Table 2]

Pb _{0.9} Sr _{0.1} (Mg _{1/3} Nb _{2/3}) A Ti ₈ ZrCO ₃₊₇ Fe ₂ O ₃									
No.	y	A	B	C	平均粒径 μm	ε/ε ₀	k _p %	d ₃₁ × 10 ⁻¹⁰ m/V	平均结晶径 μm
* 1	0	0.255	0.38	0.365	0.37	5130	63.7	-3.06	2.5
* 2	0.05	0.255	0.38	0.365	0.36	5420	64.9	-3.38	2.4
* 3	0.1	0.255	0.38	0.365	0.33	5360	65.2	-3.40	2.9
* 4	0.15	0.255	0.38	0.365	0.39	5270	64.7	-3.29	2.1
* 5	0.2	0.255	0.38	0.365	0.37	5120	62.5	-3.27	2.5
* 6	0.25	0.255	0.38	0.365	0.36	5050	61.5	-3.02	2.4
* 7	0.1	0.255	0.4	0.345	0.37	5150	58.2	-2.25	2.5
* 8	0.1	0.255	0.37	0.375	0.37	3850	61.7	-2.35	2.5
* 9	0.1	0.255	0.365	0.38	0.36	3160	59.6	-1.74	2.4

[0034] Improvement in a piezo-electric property is found rather than No.1 of the presentation with the single electrostrictive ceramics of No.2-No.9 of this example so that clearly from (Table 2). In this example, the mean particle diameter to which particle size distribution was adjusted uses pulverized coal 0.4 micrometers or less, and it is Fe 2O3 further. By adding, it can calcinate at 1200-degree C low temperature, and the property of electrostrictive ceramics is improving greatly by having controlled the fine structure.

[0035] (Example 3) They are PbO, SrCO₃, MgO, Nb₂O₅, TiO₂, and ZrO₂ as raw material powder. It uses and was made for a presentation to become as for it to be shown in the 3rd table. Pure water and a dispersant were added to the mixed fine particles blended with the predetermined presentation, it considered as the slurry, and preferential grinding was performed using the medium stirrer mill. Each presentation is 0.2, measuring the mean particle diameter after preferential grinding with a laser type particle diameter measuring instrument. μm It was made to become below. Temporary quenching of the obtained mixed powder was carried out for 2 hours. Furthermore, using the medium stirrer mill, with the zirconia ball with a diameter of 0.6mm, the dispersant and water of an organic system were added and it ground in mean particle diameter of about 0.4 micrometers or less. Grinding from which the mean particle diameter to which grinding is not progressing for the example of a comparison differs was also performed. This was dried and the raw material powder before sintering was

obtained. This powder was mixed with the organic binder, the 500-micrometer screen was passed, and the particle size regulation was carried out. The disc-like Plastic solid with a diameter [of 13mm] and a thickness of about 1mm was produced for these fine particles using metal mold, this was calcinated with the electric furnace for 2 hours, and electrostrictive ceramics was produced. A temperature up and a temperature fall rate are 300 degrees C/h. Next, the vacuum evaporatio electrode of Cr-Au is respectively given to both sides of a sample, and it is 3kV/mm between two electrodes in a 120-degree C silicone oil after that. Direct-current electric field were impressed for 30 minutes, polarization processing was carried out and the piezoelectric device was obtained. About this sample, the piezo-electric property was measured, and the fine structure was observed from the SEM photograph, and distribution of the diameter of crystal grain was searched for by the intercepting method. A measurement result is shown in (Table 3).

[0036]

[Table 3]

$Pb_{1-x} Sr_x (Ni_{1/3} Nb_{2/3})_A Ti_B Zr_C O_3$									
No.	x	A	B	C	平均粒径 μm	ϵ/ϵ_0	k_p %	$d_{31} \times 10^{-10}$ m/V	平均晶粒径 μm
* 1	0	0.4	0.38	0.22	0.15	4610	62.1	-3.08	2.7
* 2	0	0.45	0.365	0.185	0.12	5510	57.1	-2.78	2.3
* 3	0	0.45	0.360	0.190	0.15	5190	67.0	-3.53	2.0
* 4	0	0.45	0.355	0.195	0.14	6200	63.4	-3.48	2.6
* 5	0	0.45	0.350	0.200	0.15	5950	66.2	-3.66	2.0
6	0	0.45	0.350	0.200	1.2	5190	61.2	-3.03	5.5
* 7	0	0.45	0.345	0.205	0.16	5680	59.7	-3.03	2.8
* 8	0.02	0.45	0.375	0.37	0.16	4570	66.2	-3.02	2.4
* 9	0.05	0.45	0.37	0.375	0.17	3850	63.2	-2.35	2.5
10	0.07	0.45	0.365	0.38	0.16	3160	60.6	-1.74	2.4
11	0	0.475	0.165	0.360	2.9	5120	55.6	-2.63	6.3
12	0	0.475	0.170	0.355	2.8	5410	57.8	-2.89	6.3
13	0	0.475	0.175	0.350	2.6	5710	60.2	-3.23	6.1
14	0	0.475	0.180	0.345	2.7	5480	63.7	-3.37	5.8
15	0	0.475	0.185	0.340	3.1	4560	63.7	-3.02	6.1
16	0	0.475	0.190	0.335	3.0	3850	60.2	-2.51	5.9
17	0	0.475	0.195	0.330	3.2	3330	56.5	-2.13	6.2
18	0	0.475	0.200	0.325	3.2	2780	55.2	-1.85	6.2
*19	0	0.475	0.180	0.345	0.22	6420	66.3	-3.82	2.8
*20	0	0.5	0.175	0.325	0.28	6820	64.3	-3.77	2.9

[0037] Improvement is found also about No.1-No.5 of the presentation with the same electrostrictive ceramics of this example, No.7-No.9 and No.19, and which piezo-electric property of 20 so that clearly from (Table 3). In this example, when the mean particle diameter to which particle size distribution was adjusted

uses pulverized coal 0.4 micrometers or less, it can calcinate at 1200-degree C low temperature, and when the fine structure controlled, the property of electrostrictive ceramics is improving greatly. It does not pulverize, but crystal particle diameter is set to 5 micrometers or more, and the burning temperature of each example of a comparison which cannot be controlling the fine structure is also high, and it is not good. [of a property]

[0038] (Example 4) They are PbO, SrCO₃, MgO, Nb₂O₅, TiO₂, and ZrO₂ as raw material powder. It uses and was made for a presentation to become as for it to be shown in the 4th table. Pure water and a dispersant were added to the mixed fine particles blended with the predetermined presentation, it considered as the slurry, and preferential grinding was performed using the medium stirrer mill. Each presentation is 0.2, measuring the mean particle diameter after preferential grinding with a laser type particle diameter measuring instrument. It was made to become below. Temporary quenching of the obtained mixed powder was carried out for 2 hours. Furthermore, using the medium stirrer mill, with the zirconia ball with a diameter of 0.6mm, the dispersant and water of an organic system were added and it ground in mean particle diameter of about 0.4 micrometers or less. Grinding from which the mean particle diameter to which grinding is not progressing for the example of a comparison differs was also performed. This was dried and the raw material powder before sintering was obtained. This powder was mixed with the organic binder, the 500-micrometer screen was passed, and the particle size regulation was carried out. The disc-like Plastic solid with a diameter [of 13mm] and a thickness of about 1mm was produced for these fine particles using metal mold, this was calcinated with the electric furnace for 2 hours, and electrostrictive ceramics was produced. A temperature up and a temperature fall rate are 300 degrees C/h. Next, the vacuum evaporative electrode of Cr-Au is respectively given to both sides of a sample, and it is 3kV/mm between two electrodes in a 120-degree C silicone oil after that. Direct-current electric field were impressed for 30 minutes, polarization processing was carried out and the piezoelectric device was obtained. About this sample, the piezo-electric property was measured, and the fine structure was observed from the SEM photograph, and distribution of the diameter of crystal grain was searched for by the intercepting method. A measurement result is shown in (Table 4).

[0039]

[Table 4]

Pb (Ni _{1/3} Ta _{2/3}) _A Ti _B Zr _C O ₃									
No.	x	A	B	C	平均粒径 μm	ϵ/ϵ_0	k_p %	$d_{31} \times 10^{-10}$ m/V	平均压电性 μm
* 1	0	0.450	0.350	0.200	3.3	9700	24.7	-1.34	6.4
* 2	0	0.400	0.382	0.218	3.5	5520	55.7	-3.16	6.3
* 3	0	0.375	0.398	0.227	3.5	4530	54.9	-3.04	6.7
* 4	0	0.350	0.414	0.236	3.4	3540	54.5	-2.16	6.1
* 5	0	0.300	0.445	0.255	3.6	1960	44.7	-1.09	6.2
* 6	0	0.380	0.405	0.215	3.4	5890	52.3	-2.45	6.5
* 7	0	0.380	0.400	0.220	3.6	6740	52.6	-2.85	6.4
* 8	0	0.380	0.395	0.225	3.9	6520	55.8	-2.94	6.2
* 9	0	0.380	0.390	0.230	3.5	6190	53.8	-2.86	6.4
*10	0	0.380	0.385	0.235	3.8	4420	46.0	-2.74	6.3
*11	0	0.450	0.350	0.200	0.35	9700	27.6	-1.59	2.8
*12	0	0.400	0.382	0.218	0.32	6010	57.8	-3.41	2.3
*13	0	0.375	0.398	0.227	0.35	5190	59.2	-3.29	2.6
*14	0	0.350	0.414	0.236	0.34	4150	55.7	-2.42	2.8
*15	0	0.300	0.445	0.255	0.35	2460	47.7	-1.36	2.4
*16	0	0.380	0.405	0.215	0.32	6600	53.9	-2.75	2.9
*17	0	0.380	0.400	0.220	0.36	7340	55.9	-3.10	2.3
*18	0	0.380	0.395	0.225	0.36	7110	58.3	-3.23	2.5
*19	0	0.380	0.390	0.230	0.37	6830	58.0	-3.15	2.6
*20	0	0.380	0.385	0.235	0.36	4980	50.6	-2.20	2.4

[0040] It is No.10 -No.20 of this example so that clearly from (Table 4). Electrostrictive ceramics is No.1-No.10 of which the same presentation. Improvement in a piezo-electric property is found as compared with electrostrictive ceramics. In this example, when the mean particle diameter to which particle size distribution was adjusted uses pulverized coal 0.4 micrometers or less, it can calcinate at low temperature and the property of electrostrictive ceramics is improving greatly by having controlled the fine structure.

[0041] (Example 5) They are PbO, SrCO₃, MgO, Nb₂O₅, TiO₂, and ZrO₂ as raw material powder. It uses and was made for a presentation to become as for it to be shown in the 5th table. Pure water and a dispersant were added to the mixed fine particles blended with the predetermined presentation, it considered as the slurry, and preferential grinding was performed using the medium stirrer mill. Each presentation is 0.2, measuring the mean particle diameter after preferential grinding with a laser type particle diameter measuring instrument. μm It was made to become below. Temporary quenching of the obtained mixed powder was carried out for 2 hours. Furthermore, using the medium stirrer mill, with the zirconia ball with a diameter of 0.6mm, the dispersant and water of an organic system were added and it ground in mean particle diameter of about 0.4 micrometers or less. Grinding from which the mean particle diameter to which

grinding is not progressing for the example of a comparison differs was also performed. This was dried and the raw material powder before sintering was obtained. This powder was mixed with the organic binder, the 500-micrometer screen was passed, and the particle size regulation was carried out. The disc-like Plastic solid with a diameter [of 13mm] and a thickness of about 1mm was produced for these fine particles using metal mold, this was calcinated with the electric furnace for 2 hours, and electrostrictive ceramics was produced. A temperature up and a temperature fall rate are 300 degrees C/h. Next, the vacuum evaporationno electrode of Cr-Au is respectively given to both sides of a sample, and it is 3kV/mm between two electrodes in a 120-degree C silicone oil after that. Direct-current electric field were impressed for 30 minutes, polarization processing was carried out and the piezoelectric device was obtained. About this sample, the piezo-electric property was measured, and the fine structure was observed from the SEM photograph, and distribution of the diameter of crystal grain was searched for by the intercepting method. A measurement result is shown in (Table 5).

[0042]

[Table 5]

Pb _{1-x} Sr _x (Mg _{1/3} Nb _{2/3}) _A (Ni _{1/3} Nb _{2/3}) _B Ti _C Zr _D O ₃										
No.	x	A	B	C	D	平均粒径 μm	ϵ/ϵ_0	k_p %	$d_{31} \times 10^{-10}$ m/V	平均晶粒 μm
* 1	0.02	0.05	0.35	0.35	0.25	0.35	5210	64.1	-3.45	2.7
* 2	0.04	0.10	0.21	0.35	0.34	0.32	5550	64.6	-3.53	2.3
* 3	0.06	0.15	0.14	0.36	0.35	0.35	5860	65.5	-3.58	2.0
* 4	0.08	0.20	0.07	0.36	0.37	0.34	5970	66.4	-3.60	2.6
Pb _{1-x} Sr _x (Mg _{1/3} Nb _{2/3}) _A (Ni _{1/3} Ta _{2/3}) _B Ti _C Zr _D O ₃										
* 5	0.02	0.05	0.35	0.38	0.22	0.35	5880	60.8	-3.32	2.7
* 6	0.04	0.10	0.21	0.38	0.31	0.32	5510	62.5	-3.28	2.5
* 7	0.06	0.15	0.14	0.38	0.33	0.35	5350	63.0	-3.23	2.6
* 8	0.08	0.20	0.07	0.38	0.35	0.34	5140	63.4	-3.11	2.9
Pb _{1-x} Sr _x (Ni _{1/3} Nb _{2/3}) _A (Ni _{1/3} Ta _{2/3}) _B Ti _C Zr _D O ₃										
* 9	0	0.05	0.35	0.35	0.30	0.35	6510	59.4	-3.61	2.3
*10	0	0.10	0.21	0.35	0.34	0.32	6210	61.7	-3.58	2.4
*11	0	0.15	0.14	0.35	0.36	0.35	5990	62.9	-3.56	2.3
*12	0	0.20	0.07	0.36	0.37	0.34	5700	63.6	-3.55	2.7

[0043]When the mean particle diameter to which particle size distribution was adjusted uses pulverized coal 0.4 micrometers or less in this example from (Table 5), it can calcinate at low temperature and the property is improving greatly from the conventional property by having controlled the fine structure.

[0044]

[Effect of the Invention]As mentioned above, the piezo-electric property of electrostrictive ceramics can be raised by reducing burning temperature by pulverizing by the medium stirrer mill, and controlling the fine structure by electrostrictive ceramics of this invention.

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